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Intra- and inter-annual uranium concentration variability in a Belizean stalagmite controlled by prior aragonite precipitation: a new tool for reconstructing hydro-climate using aragonitic speleothems

Robert A. Jamieson ^{a,*}, James U.L. Baldini ^a, Marianne J. Brett ^{a, b}, Jessica Taylor ^a, Harriet E. Ridley ^a, Chris J. Ottley ^a, Keith M. Prufer ^c, Jasper A. Wassenburg ^d, Denis Scholz ^d, Sebastian F. M. Breitenbach ^e

^a Department of Earth Sciences, Durham University, United Kingdom

^b Royal Holloway University, London, United Kingdom

^c Department of Anthropology, University of New Mexico, United States of America

^d Institute for Geosciences, Johannes Gutenberg University, Mainz, Germany

^e Department of Earth Sciences, University of Cambridge, United Kingdom

* Corresponding author at: Department of Earth Sciences, Durham University, United Kingdom. E-mail address: r.a.jamieson@durham.ac.uk

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Abstract

Aragonitic speleothems are increasingly utilised as palaeoclimate archives due to their amenability to high precision U-Th dating. Proxy records from fast-growing aragonitic stalagmites, precisely dated to annual timescales, can allow investigation of climatic events occurring on annual or even sub-annual timescales with minimal chronological uncertainty. However, the behaviour of many trace elements, such as uranium, in aragonitic speleothems has not thus far been as well constrained as in calcitic speleothems. Here, we use uranium concentration shifts measured across primary calcite-to-aragonite mineralogical transitions in speleothems to calculate the distribution coefficient of uranium in aragonitic speleothems (derived $D_U = 3.74 \pm 1.13$). Because our calculated D_U is considerably above 1 increased prior aragonite precipitation due to increased karst water residence time should strongly control stalagmite aragonite U/Ca values. Consequently, uranium concentrations in aragonitic speleothems should act as excellent proxies for effective rainfall.

We test this using a high-resolution ICP-MS derived trace element dataset from a Belizean stalagmite. YOK-G is an aragonitic stalagmite from Yok Balum cave in Belize with an extremely robust monthly-resolved chronology built using annual $\delta^{13}\text{C}$ cycles. We interpret seasonal U/Ca variations in YOK-G as reflecting changes in the amount and seasonality of prior aragonite precipitation driven by variable rainfall amounts. The U/Ca record strongly suggests that modern drying has occurred in Belize, and that this drying was primarily caused by a reduction in wet season rainfall. This is consistent with published stable isotope data from YOK-G also very strongly suggesting modern rainfall reductions, previously interpreted as the result of southward ITCZ displacement. Our results strongly suggest that U/Ca values in aragonitic speleothems are excellent proxies for rainfall variability. This new tool, combined with the exceptional chronological control characteristic of aragonitic stalagmites and the high spatial resolution afforded by modern microanalytical techniques, should facilitate the construction of new exquisitely resolved rainfall records, providing rare insights into seasonality changes as well as long-term changes in local recharge conditions.

1.1 Introduction

Speleothems are invaluable continental paleoclimate archives that are amenable to precise and accurate U-Th dating, and can yield high-resolution proxy records. Speleothem-based climate reconstructions are particularly useful for reconstructing effective rainfall, and can provide diverse information about rainfall, including moisture source and trajectory, rainfall amount, seasonality, and karst residence time (Fairchild et al., 2006). Well-established stable isotope proxies retain each of these variables to varying degrees in different stalagmites. Disentangling these effects in a given sample is challenging, with individual proxies such as $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ potentially reflecting multiple climatological and environmental factors in a single proxy record. Therefore, considering multi-proxy approaches when attempting to reconstruct effective rainfall from speleothem records is critical. Trace element proxies for prior carbonate precipitation and/or residence time reflect the volume of water infiltrating through the karst and can help deconvolve these separate signals. In calcite speleothems, the most commonly used trace element proxy for prior calcite precipitation (PCP) is Mg/Ca (Fairchild and Treble, 2009), due to its abundance and strong partitioning between fluid and solid phases (Fairchild et al., 2000). Other element ratios such as Sr/Ca or Ba/Ca also produce complementary information about hydrology (McDonald et al., 2007). In addition, sulphate concentrations in speleothems have been used as tracers of volcanic or anthropogenic inputs to the karst system (Borsato et al., 2015; Frisia et al., 2005; Wynn et al., 2008; Wynn et al., 2010; Wynn et al., 2014). Elements that are less water soluble or less easily incorporated into the calcite crystal lattice, although utilised more rarely, are useful proxies for volcanic or anthropogenic inputs into the

karst system (Jamieson et al., 2015) or as chronological markers of seasonal flushing of associated organic material (Borsato et al., 2007; Hartland et al., 2012). Similar mechanisms control trace elements in aragonitic speleothems, although the differing crystal structure of aragonite compared to that of calcite means that elements are incorporated differently between the two minerals. Aragonitic speleothems are particularly useful in paleoclimatic research because their generally high uranium content allows very high U-Th dating precision (Denniston et al., 2013; Kennett et al., 2012; Woodhead et al., 2012). Despite this potential, the relative scarcity of published aragonitic stalagmite trace element records (Finch et al., 2003; Tan et al., 2014; Wassenburg, 2013) means that trace element partitioning behaviour into their structure remains poorly understood. Research constraining uncertainties in elemental behaviour in aragonitic stalagmite is therefore crucial.

1.2 Prior Aragonite Precipitation

Prior calcite precipitation is a significant control on drip water element concentrations before trace element incorporation in speleothems (Fairchild et al., 2001; Fairchild et al., 2000; Fairchild and Treble, 2009; Treble et al., 2015). Precipitation of calcium carbonate up-flow from the speleothem will either increase or decrease the concentrations of various trace elements in dripwaters (and thus speleothems) depending on the value of their distribution coefficients. This mechanism controls a significant proportion of variability in water-soluble alkaline earth metal concentrations due to their abundance and predictable behaviour. PCP is not a primary control on other elemental variations due to the dominance of other processes such as supply, transport, and/or growth/crystal structure dependencies for incorporation (e.g. pH Wynn et al. (2014) or growth rate Fairchild et al. (2001)). Far less is known about the effects of prior aragonite precipitation (PAP) on speleothem geochemistry. However, PAP probably significantly influences speleothem geochemistry in environments where aragonite precipitation is favoured, though currently very few studies have considered PAP controls on speleothem geochemistry. Fairchild and Treble (2009) discussed the potential of PAP as an influence on Sr/Ca, but concluded that it would have a minimal effect on strontium concentrations. Wassenburg et al. (2012) highlighted the potential for PAP to increase dripwater Mg/Ca, and a lack of PCP as an explanation for the decoupling of Sr, Mg and Ba within speleothem aragonite. Wassenburg et al. (2013) identified PAP from monitored drip waters by observing a negative correlation between Mg and Sr concentrations. These studies established PAP as a process that can affect dripwater and/or speleothem trace element concentrations, but did not propose a diagnostic elemental proxy for PAP. The potential of PAP to function as an important hydrologically mediated control on speleothem geochemistry merits further consideration, especially considering that the differing crystal structure of aragonite compared to calcite may favour the incorporation of elements

with larger ionic radii, thereby providing proxies for environmental changes that are not available in calcite speleothems. One element incorporated in greater concentrations in aragonite because of the aforementioned reasons is uranium, which is mostly incorporated as $\text{UO}_2(\text{CO}_3)_3$ (Reeder et al., 2000) and readily substitutes for Ca within the aragonite crystal structure but less so in that of calcite.

U/Ca has not previously been used extensively in speleothem studies as a proxy for paleoenvironmental information, however several groups have measured U/Ca or $^{234}\text{U}/^{238}\text{U}$ activity ratios in calcite speleothems and discussed the source and mechanisms of incorporation. Bourdin et al. (2011) suggested that uranium in dripwaters is primarily derived from limestone dissolution at their study site, with its incorporation in calcite depending on crystallographic factors such as the presence of kinks or lattice defects. Other groups have suggested that uranium can be derived from an external source such as Saharan dust (Frumkin and Stein, 2004), overlying sediments (Zhou et al., 2005), or anthropogenic sources/disruption (Siklosy et al., 2011). In addition, PCP has been discussed as a possible influence on drip water U/Ca (Johnson et al., 2006). In summary, very few studies have discussed uranium in detail as a proxy and, to our knowledge, none in aragonitic speleothems.

1.3 Distribution Coefficients in Speleothem Aragonite and Calcite

One of the key limitations in quantitative speleothem trace element research is imprecise knowledge of the distribution coefficients (D_{TE}) controlling the incorporation of elements in speleothems. Existing studies of distribution coefficients in both calcite and aragonite are often non-speleothem specific, and can include biological effects not present in stalagmites (corals), non-comparable fluids (seawater, or other high ionic strength solutions), or implausible growth rates or temperatures (Busenburg and Plummer, 1985; DeCarlo et al., 2015; Meece and Benninger, 1993; Swart and Hubbard, 1982). As such, the applicability of these values to speleothem science is extremely limited.

Recent studies have determined distribution coefficients for speleothem calcite based on karst analogue experiments (Day and Henderson, 2013), or using in-situ measurements of dripwaters and precipitates (Tremaine and Froelich, 2013). These values are more applicable to speleothem studies than earlier efforts, but distribution coefficients are not absolute constants. Instead, distribution coefficients depend on a variety of factors including: temperature, growth rate, competition effects (i.e., solution composition), pH, biological factors, elemental form (e.g., valence state, complexation, etc.), crystallography, and many others (Gabitov et al., 2008; Gabitov et al., 2014; Huang and Fairchild, 2001; Meece and Benninger, 1993; Mucci and Morse, 1983). It is thus likely that cave- or

drip-specific distribution coefficient values exist. The concept of a distribution coefficient does have value for understanding trace element partitioning in a general sense, but is not an absolute constraint on trace element variability in speleothems.

In practice, the key piece of information for interpreting speleothem trace element data in terms of PCP and/or PAP is whether the distribution coefficient is greater than or less than one, that is, whether it is preferentially included or excluded from the mineral phase. Even this binary distinction is within the range of estimates for some elements in aragonite within the previously published literature (Figure 1); therefore defining clear ranges for these values in speleothems is critical. Without better estimates of these values, it is not possible to determine whether elemental concentrations would increase or decrease in response to increasing amounts of PAP.

Uranium is abundant in aragonitic speleothems but lacks a well-constrained distribution coefficient value. Existing studies generally suggest that uranium is preferentially incorporated into aragonitic stalagmites ($D_U > 1$) and excluded from calcitic stalagmites ($D_U < 1$) (Denniston et al., 2013). If the values of D_U are indeed either side of one in the two mineral phases then uranium represents an ideal geochemical parameter to diagnose the presence, dominance, or variability of PAP as a control on stalagmite geochemistry. PAP variability is (like PCP variability) likely controlled by recharge variability, and may therefore allow U/Ca to function as a palaeorainfall proxy in karst environments where aragonite precipitation occurs. This study is the first to investigate the systematics of U/Ca in an aragonitic speleothem as a proxy for PAP and, in conjunction with $\delta^{13}\text{C}$, to use these geochemical indicators to reconstruct past rainfall variability and seasonality.

2.0 Yok Balum cave site description

Yok Balum cave in southern Belize (16° 12' 30.78" N, 89° 40' 24.42" W; 366m above sea level) is a well monitored tropical cave developed in a SW-to-NE trending karst ridge composed of Campur Formation limestone in the Toledo district of southern Belize. The cave is well studied, with cave monitoring records (Ridley et al., 2015b) as well as stable isotope records from two stalagmites already published (Kennett et al., 2012; Ridley et al., 2015a). Here, we supplement these existing records, particularly the YOK-G $\delta^{13}\text{C}$ record of Ridley et al. (2015a), with complementary trace element data.

The cave consists of a single main trunk passage approximately 540m in length with two entrances. These entrances are a small eastern opening and a larger, higher opening to the southwest formed by a cave roof collapse. The cave ventilates daily through these two entrances, ensuring that CO_2 concentrations in the cave never rise to a level where dissolution of carbonate speleothems would

occur. The cave is developed in a tectonically active area, and field observations suggest that it may have formed tracking a local fault. The stalagmite YOK-G was collected in 2006 from an actively dripping area of the cave approximately 80m from the smaller eastern entrance.

Southern Belize has a tropical climate, with seasonal temperatures only ranging approximately 4°C about the annual mean of 22.8°C. Latitude and elevation control rainfall distribution in Belize, with total annual rainfall ranging from 1300mm in the north to 4500mm in the south. Rainfall in the region exhibits a strong seasonality with >80% of the annual rainfall occurring between June and September in the peak of the May-January wet season. February to April receives significantly less rainfall, with evaporation greatly reducing soil and karst infiltration (Kennett et al., 2012).

3.0 Methods

3.1 Sample preparation and analysis

For analyses approximately 250µg of speleothem material was milled at 100µm resolution using a computer-controlled ESI/New Wave Micromill, equipped with a 0.8mm tungsten carbide drill bit. Powders were dissolved in 1% Nitric Acid (PWR 67% Nitric Acid Ultrapure Normatom for trace element analysis, diluted with Milli-Q water) and a suite of elements measured using a Thermo Scientific X Series II inductively-coupled plasma mass spectrometer (ICP-MS) at Durham University. The milled analyte used in this analysis is an aliquot of the larger milled volume; the remainder was used for stable isotope measurements (Ridley et al., 2015a), thereby allowing direct comparison with no chronological error between the proxies.

A set of multi-elemental Romil standards and blanks re-run throughout the sequence of samples allow precise quantification and correction for machine drift. Analytical precision on individual samples was <5% RSD for Ca, Mg and U, with Ca precision generally <2% RSD (3 repeat measurements). Detection limits varied by run, but were generally <0.1ppb for Mg and Ca, and <1ppt for U.

Stable isotope analyses were conducted at Durham University using a Thermo-Finnigan MAT 253 Isotope-Ratio Mass Spectrometer coupled with a Gasbench II, external precision of 0.05-0.1‰ as detailed in Ridley et al. (2015a). Each batch of fifty sample aliquots was run alongside 14 standard powders; NBS18 (carbonatite), NBS19 (limestone), LS VEC (lithium carbonate) and an internal laboratory standard DCSO1. Normalisations and corrections were made to NBS19 and LS VEC. Random samples were re-run to ensure reproducibility between the runs and lend confidence to the results. Values reported are relative to the international VPDB standard.

Clear annual cycles in the monthly resolved $\delta^{13}\text{C}$ dataset, anchored to 1955 by detecting the radiocarbon 'bomb spike', were used to construct the monthly-resolution stalagmite age model. Eighteen high-precision U-Th dates produced at the University of New Mexico Radiogenic Isotope Laboratory fall within error of the cycle counting age model confirming the independent chronology. Specifics of the dating and age model construction are detailed in Ridley et al. (2015a). The stalagmite was actively dripping at the time of collection; however, reliable $\delta^{13}\text{C}$ cycles are only present until 1982 (approximately 8mm from the stalagmite top). The reasons for this are unclear, and may reflect a cessation or slowdown in growth after 1982, possibly linked to the proximal El Chichón eruption, which is approximately synchronous with this change. Therefore, post-1982 measurements are not considered because of lack of adequate chronological control.

3.2 Empirical calculation of distribution coefficients in speleothems

We present a method to calculate D_{ij}^a from speleothem calcite to aragonite transitions. Our approach is similar to the method described by Wassenburg et al. (In Revision), who also provide speleothem aragonite distribution coefficients for Mg, Sr and Ba. Wassenburg et al. (In Revision) also provide and discuss in detail the uncertainty of the resulting aragonite distribution coefficient taking into account, among other factors, potential changes in the chemical composition of the dripwater through time.

The calculations of the aragonite distribution coefficients involves two-steps: Firstly, a fluid concentration is calculated using the known uranium distribution coefficient for calcite together with the measured uranium concentration in a calcite layer. Secondly, the calculated fluid value, together with the measured uranium concentration in the aragonite layer, is then used to calculate the distribution coefficient between the fluid and aragonite (Figure 2). The uranium distribution coefficient for calcite used here is calculated from the temperature dependent equation of Day and Henderson (2013) ($D_{ij}^c = 0.14e^{(-0.025*T)}$) and mean annual temperature within each studied cave.

This approach operates on the assumption that the U/Ca in the fluid have not changed significantly between the precipitation of the two mineral phases. To minimise the potential effect of variable fluid concentrations we have used values from as close together as are available in the stalagmite, but this does not preclude the possibility of small changes in concentration because of hydrological or climatological variations. This concern can be somewhat ameliorated by examining layers with lateral changes in mineralogy such as those documented by Wassenburg et al. (2012). This approach is more robust as the mineral phases precipitated from the same drip, with only very small changes in fluid chemistry occurring laterally as the minerals precipitate. We calculate several uranium

distribution coefficient values in aragonite (D_{ij}^a) using this method from speleothems with both lateral and vertical transitions between mineral phases (McDermott et al., 1999; Railsback et al., 2011; Wassenburg, 2013; Wassenburg et al., 2012; Wassenburg et al., 2013). Any speleothems for which petrographic analysis suggests diagenetic alteration (e.g. Green et al. (2015)) are omitted from this analysis due to the recrystallized phase potentially precipitating from a markedly different fluid composition (Perrin et al., 2014).

4.0 Results

4.1 Stable Isotope and Trace Element Results

From 1669-1983 AD, the YOK-G $\delta^{13}\text{C}$ record shows a long term trend towards more positive values, with a shift of approximately 0.5-1‰ in the long term mean over that interval (Figure 3).

Superimposed on this trend are decadal-scale $\delta^{13}\text{C}$ fluctuations of between 0.5-1‰, as well as cyclical intra-annual (seasonal) variability of up to 1‰. U/Ca shows a decrease in the long-term mean from approximately 2×10^{-5} to 1×10^{-5} from 1669-1983 AD, with several decadal scale fluctuations of similar magnitude. Like $\delta^{13}\text{C}$, U/Ca shows annual cycles, with U/Ca cycle amplitudes of approximately 0.2×10^{-5} - 0.5×10^{-5} . Annual U/Ca cycles are generally anti-correlated with those of $\delta^{13}\text{C}$, although not exclusively so. The mean annual values of $\delta^{13}\text{C}$ and U/Ca anti-correlate throughout the record (1669-1983; $r = -0.70$, $p < 0.0001$).

Mg/Ca values in YOK-G show a very low magnitude long-term decrease in baseline values. Annual spikes of up to 0.0007 above the 0.0001 baseline occur during the wet season, anti-correlated with the annual cycles in $\delta^{13}\text{C}$.

4.2 Uranium Distribution Coefficients

The calculated values for D_{ij}^a are summarised in Figure 2 and Table 1, where calculations using both vertical and lateral transitions show similar value ranges for D_{ij}^a of 1.8-4.5. Our preferred value for D_{ij}^a calculated from this study is 3.74 ± 1.13 , as the mean value \pm one standard deviation of the two lateral calcite-aragonite transitions used. This value should not be considered an absolute value for the reasons discussed in section 1.3. However, it provides a useful approximation for modelling and confirms that the value in aragonitic speleothems is greater than one. Wassenburg et al. (in review) use a similar approach using additional speleothem transitions and report a similar range of distribution coefficients (6.26 ± 4.54). As our calculated values also fall within this range, we can confidently assert that the D_{ij}^a value in speleothem aragonite is greater than one.

5.0 Discussion

5.1 General Trends in U/Ca and $\delta^{13}\text{C}$

In general, $\delta^{13}\text{C}$ in aragonitic speleothems and in systems where PAP is occurring will behave very similarly to the calcite equivalents. Whilst the exact value of the fractionation factor between precipitated aragonite and bicarbonate in solution may vary slightly from that of calcite, progressive precipitation will still act to increase the $\delta^{13}\text{C}$ of the solution (Fairchild et al., 2006; Polag et al., 2010). As a result, PAP and PCP will both lead to higher $\delta^{13}\text{C}$ values in speleothems. Ridley et al. (2015a) interpreted $\delta^{13}\text{C}$ values in YOK-G as a palaeorainfall proxy, and noted both a strong intra-annual signal corresponding to seasonality as well as long-term variations resulting from intertropical convergence zone position (ITCZ) shifts linked to anthropogenic and natural (volcanic) aerosol forcing. The $\delta^{13}\text{C}$ record shows an increasing drying trend post-1850, which is expressed in both the overall $\delta^{13}\text{C}$ signal and particularly in the wet season $\delta^{13}\text{C}$ values. This multi-proxy inferred drying trend mirrors the observed decrease in annual rainfall in several meteorological stations near Yok Balum cave (Ridley et al., 2015a).

5.2 Uranium Distribution Coefficients

Lateral transition values are the basis for our preferred value as they result from small changes in dripwater concentrations due to mineral precipitation rather than potentially large shifts vertically due to changes in climate or flow path, which may result in competition effects modifying the D_{U}^{a} value. The range of these values may result from variations in U/Ca in the dripwaters between the precipitation of the two phases (e.g. due to prior carbonate precipitation or varying dissolution) producing variable errors in the calculated D_{U}^{a} values. Alternatively, they may be truly different D_{U}^{a} values in each stalagmite stemming from the various other factors which influence distribution coefficients (e.g. growth rates Gabitov et al. (2008) or dripwater pH Wassenburg et al. (In Revision)). Similarly high values have been found experimentally (Meece and Benninger, 1993) and in speleothem samples (Wassenburg et al., in review). However, because these values are all greater than one they indicate that uranium is preferentially incorporated into speleothem aragonite. This is consistent with the general understanding of the uranium incorporation mechanism into the crystal lattice. In aragonite the most common aqueous uranium species, $\text{UO}_2(\text{CO}_3)_3^{4-}$, is incorporated into the crystal structure intact, whilst to be incorporated into calcite the co-ordination of this unit has to change (Reeder et al., 2000). This suggests that the distribution coefficients established here are consistent with both the known crystallographic incorporation mechanism, and the generally higher observed concentrations of uranium in aragonitic speleothems. We can conclude that PAP would result in lowered U/Ca values in dripwater, and thus lower stalagmite concentrations, during drier conditions.

5.3 Intra-annual variations and inferred controls on U/Ca

Mean monthly U/Ca values demonstrate the presence of a clear annual cyclicity in YOK-G, which is overall anti-correlated with annual $\delta^{13}\text{C}$ cycles (Figure 4). A mechanism must therefore operate at the YOK-G site that increases dripwater U/Ca values during wetter months of the year. Prior calcite precipitation would have the opposite effect, lowering U/Ca values during wetter months and increasing U/Ca during drier months as uranium is excluded from calcite and dripwater concentrations increase with intensified PCP. Increased residence times of infiltrating water in drier months would also tend to increase uranium concentrations as percolating waters have more time to leach trace elements from the karst rock. The D_U value of 3.74 ± 1.13 calculated above, definitively greater than one (Figure 1), confirms that PAP would result in increased U/Ca values during the wet season. As both PCP and/or increased residence times would have the opposite effect to the observed variability, we infer that PAP is the dominant control on seasonal variations in U/Ca concentrations throughout YOK-G (Figure 5).

The mean annual values of $\delta^{13}\text{C}$ and U/Ca anti-correlate throughout the record (1669-1983; $r = -0.70$, $p < 0.0001$), consistent with PAP as a dominant control on YOK-G U/Ca on inter-annual timescales. The strength of the anti-correlation between $\delta^{13}\text{C}$ and U/Ca varies interannually with some years displaying a very strong anti-correlation but others exhibiting a weaker anti-correlation or occasionally even a positive correlation (Figure 6). Overall, U and $\delta^{13}\text{C}$ are strongly anti-correlated in 121 years ($r < -0.5$), weakly anti-correlated in 76 years ($-0.5 < r < 0$), weakly positively correlated in 71 years ($0 < r < 0.5$), and strongly positively correlated in 45 years ($r > 0.5$). Positively correlated years are characterised by greatly reduced rainfall seasonality inferred by using both U/Ca and $\delta^{13}\text{C}$ (Figure 7). This suggests that in years where $\delta^{13}\text{C}$ and U/Ca are positively correlated, PAP is no longer the dominant control on the intra-annual U/Ca variability of the speleothem. Monthly and mean annual $\delta^{13}\text{C}$ and U/Ca values suggest that these years are drier than the overall mean, as well as exhibiting reduced seasonality. This reflects decreased rainfall, largely in the wet season, where $\delta^{13}\text{C}$ and U/Ca are markedly less negative and lower respectively. Therefore, we can infer that in years with reduced wet season rainfall, the dominance of seasonal PAP control on YOK-G geochemistry breaks down because of increased residence time (and thus bedrock dissolution) becoming a more dominant control or simply because of reduced seasonal rainfall contrasts. During drier years increased PAP is still occurring, resulting in lower U/Ca values in those years, it simply does not display the strong seasonal pattern observed in wetter/more seasonal years.

The variability of this seasonal (anti)-correlation varies through time in the stalagmite record (Figure 8), and is linked to the inferred amount of summer rainfall. Prior to ~1850, strongly seasonal, wetter,

anti-correlated years dominate the record, suggesting that in the pre-industrial period most years in Belize were characterised by strongly seasonal rainfall controlled by the earlier arrival of ITCZ rainfall. Following the mid-1800s, the frequency of years when $\delta^{13}\text{C}$ and U/Ca are positively correlated increases, reflecting reduced wet season rainfall, consistent with a more southerly ITCZ (Ridley et al., 2015a).

5.4 Comparison with meteorological records

Comparison with Punta Gorda rainfall station records (1906-1983) from approximately 30km to the southeast further supports the link between the annual $\delta^{13}\text{C}$ versus U/Ca correlation with seasonality. Maximum monthly rainfall and the difference between maximum and minimum monthly rainfall (both measures of rainfall seasonality, because minimum monthly rainfall is reasonably consistent through the record) both anti-correlate with the U/Ca vs $\delta^{13}\text{C}$ annual correlation value ($r = -0.26$, $p = 0.03$ and $r = -0.27$, $p = 0.02$ respectively). In other words, years with greater wet season rainfall and increased seasonality resulted in a stronger negative correlation between U/Ca and $\delta^{13}\text{C}$, and years with less wet season rainfall and reduced seasonality exhibit a positive correlation because seasonal PAP shifts are muted and consequently is no longer a dominant control on seasonal U/Ca variability. We suggest that this diminished seasonality is enough that residence time and bedrock interaction effects (which positively correlate with $\delta^{13}\text{C}$) overwhelm the lower amplitude seasonal U/Ca variability signal. PAP is still occurring, and indeed is likely intensified in these drier years, however it exhibits reduced variability on intra-annual timescales due to the reduced seasonality. Consequently, dry years have a lower mean U/Ca value due to increased PAP, but positively correlate intra-annually with $\delta^{13}\text{C}$ due to reduced variability in PAP (Figure 9).

5.5 Comparison of proxies with long-term climate records

In the Industrial Period (post-1850), $\delta^{13}\text{C}$ and U/Ca both indicate a trend of overall drying and reduced seasonality. As outlined by Ridley et al. (2015a) these variables (annual means, peak wet values, peak dry values and seasonal differences of both proxies) all correlate with increasing Northern Hemisphere Temperature (NHT) (see Table 2). Indeed U/Ca displays a stronger and more significant relationship with NHT over this period perhaps suggesting that this proxy is even more sensitive to rainfall shifts than $\delta^{13}\text{C}$.

This shift in both proxies towards drier and less seasonally variable conditions post-1850 supports the interpretation of Ridley et al. (2015a) that the northern maximum extent of the ITCZ has shifted southwards in response to increased anthropogenic sulphate aerosol emissions in the Northern

Hemisphere and changing hemispheric temperature contrasts, consequently resulting in drier wet seasons in Belize and reduced hydrological seasonality.

For the pre-industrial period the relationship with NHT is less clear, with only dry season U/Ca showing a weak ($r = -0.16$, $p = 0.003$) anti-correlation to NHT. This suggests that NHT had an influence on dry season moisture balance, possibly in the form of increased dry season evapotranspiration, but did not strongly influence wet season rainfall.

In summary, on inter-annual timescales U/Ca in YOK-G is a proxy for overall dryness in Belize, whilst the annual correlation or anti-correlation of U/Ca and $\delta^{13}\text{C}$ reflects changes in intra-annual rainfall seasonality.

5.6 Mg/Ca variability in YOK-G

Mg/Ca is a more commonly used proxy for prior carbonate precipitation in speleothems, due to its strong partitioning behaviour and abundance in karst environments. We therefore also examine the behaviour of Mg/Ca in YOK-G over the same period of the $\delta^{13}\text{C}$ and U/Ca datasets. Having established that PAP is a significant control on the geochemistry of YOK-G, this is a unique opportunity to improve our understanding of magnesium behaviour in aragonitic stalagmites.

Prior carbonate precipitation does not appear to control intra-annual Mg/Ca variability in this speleothem. Distribution coefficients for magnesium quoted in the literature are generally below one in both calcite (e.g., $D_{\text{Mg}}^{\text{c}} = 0.012\text{--}0.029$ (Day and Henderson, 2013), $D_{\text{Mg}}^{\text{c}} = 0.015\text{--}0.020$ (Fairchild et al., 2010)) and aragonite (e.g., $D_{\text{Mg}}^{\text{a}} = 0.000097 \pm 0.00009$ (Wassenburg et al., In Revision) $D_{\text{Mg}}^{\text{a}} = 0.00002 - 0.00008$ (Gabitov et al., 2008), $D_{\text{Mg}}^{\text{a}} = 0.00053 - 0.0149$ (Gaetani and Cohen, 2006)), therefore drier intervals should lead to increased stalagmite Mg concentrations, and a positive seasonal correlation with $\delta^{13}\text{C}$. However, YOK-G Mg/Ca generally peaks in the wet season, anti-correlating with $\delta^{13}\text{C}$, opposite to the predicted relationship if either PCP or PAP were the dominant controls on Mg/Ca in this stalagmite (Figure 10). We propose three possible mechanisms for this observation:

1) Elevated wet season Mg/Ca values could result from influx of magnesium rich material from the soil and epikarst during periods of increased rainfall. One candidate for this material is wood ash produced by biomass burning from slash and burn agriculture as practiced in the region. Magnesium is a significant component of wood ash (Etiégni and Campbell, 1991), and could potentially be washed in as either magnesium bearing minerals found in wood ash or as leached ions in dripwaters.

2) Times of higher rainfall and increased water volume in the karst may activate flowpaths sampling from areas of less chemically mature dolomitised limestone material where increased amounts of magnesium are dissolved from the host rock. This overflow pathway, only active during periods of increased rainfall, potentially passes through rocks with elevated magnesium content and/or less weathered surfaces. This explanation, whilst plausible, is extremely difficult to test without extensive additional site hydrology characterisation and country rock sampling within the karst.

3) Because the aragonite crystal lattice strongly excludes magnesium ($D_{Mg}^a = 0.00002 - 0.00008$ (Gabitov et al., 2008)) organic colloidal transport, clay mineral incorporation or the presence of fluid inclusions may overprint any hydrological controls on the Mg signal (Wassenburg, 2013; Wassenburg et al., 2012; Yang et al., 2015). This is consistent with the timing of the increased Mg/Ca values, as wet season rainfall would result in both increased flushing of material and potentially increased growth rates. The nature of the long-term Mg dataset, with large amplitude, but short-lived, spikes in Mg concentration superimposed on a relatively low concentration baseline supports sporadic inputs of colloidally associated Mg associated with flush events.

Regardless of the specific mechanism, Mg/Ca is clearly not an effective hydrological proxy in this stalagmite. This further reinforces the concept that the interpretation of proxy records in stalagmites as rainfall variability often requires more information than a single proxy record. Multi-proxy approaches using trace elements in conjunction with stable isotopes (this study), other trace element proxies (Wassenburg et al., 2012) , or dripwater monitoring (Rutledge et al., 2014), are vital to support any palaeoclimatic interpretation.

6.0 Conclusions

We calculate a distribution coefficient of uranium in aragonitic speleothems of 3.74 ± 1.13 , which is in agreement within error with the value derived by Wassenburg et al. (In review). We infer that prior aragonite precipitation results in lower U/Ca in speleothems. Aragonitic speleothems contain relatively high concentrations of uranium and thus have great potential to provide exceptionally precise U-Th ages. In addition, they grow in environments where varying aragonite precipitation along the flow pathway can exert a strong control on dripwater uranium content with little additional noise in the signal from varying external inputs. We therefore suggest that in aragonitic speleothems uranium concentrations are a powerful proxy for rainfall variability.

The unusually high temporal resolution of the YOK-G trace element record enables an examination of seasonal geochemical variations in aragonitic stalagmites and the development of a new proxy for rainfall. U/Ca hydrological variations occur on both intra- and inter-annual timescales, and are

therefore useful for assessing seasonal changes in rainfall patterns. We demonstrate that U/Ca correlates with other rainfall proxies such as $\delta^{13}\text{C}$, can be linked to instrumental rainfall records, correlates with other climatic variables (e.g., NHT), and reflects previously inferred trends in Belizean paleo-rainfall. Mg/Ca in YOK-G does not appear to be a viable paleo-rainfall proxy, emphasising the importance of considering multiple proxies.

The development of an additional hydrological proxy in aragonitic speleothems, which is easily measured at extremely high spatial resolution and appears extremely sensitive to rainfall amount and seasonality, is an important addition to the set of tools available with which to reconstruct climate. Aragonitic speleothems, with their precise age controls, are ideal for this purpose as they minimise age uncertainty. This study presents a valuable new method for estimating palaeo-rainfall in low-latitude regions where few high quality rainfall proxy archives are available.

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Figure Captions and Tables

Figure 1: A selection of published and newly calculated distribution coefficients for uranium in aragonite. From left to right: published values for aragonite corals in seawater (orange) and inorganic laboratory precipitation experiments (blue), calculated values for vertical transitions in speleothems (brown) and lateral transitions in speleothems (green) calculated as described in Section 4.2 (Amiel et al., 1973; DeCarlo et al., 2015; Flor and Moore, 1977; Friedman, 1968; Gabitov et al., 2008; Gvirtzman et al., 1973; McDermott et al., 1999; Meece and Benninger, 1993; Railsback et al., 2011; Sackett and Potratz, 1963; Schroeder et al., 1970; Swart and Hubbard, 1982; Thompson and Livingston, 1970; Veeh and Turekian, 1968; Wassenburg, 2013; Wassenburg et al., 2012). Published coral and experimental values are shown with the range of values reported, calculated values (this study) are shown with \pm one standard deviation of the mean of the calculated values (black). The mean value of 3.74 ± 1.13 for lateral transitions (bold circle) is our preferred value (see section 4.2).

Figure 2: Examples of vertical and lateral calcite-aragonite transitions from Wassenburg (2013) (left). Distribution coefficient calculation method used in this paper (right).

Figure 3: A: Time series plot of long-term trends in $\delta^{13}\text{C}$ (blue), U/Ca (red), Mg/Ca (green) and $\delta^{18}\text{O}$ (black). B: Expanded time series (1790-1810) showing annual cyclicity in proxy values.

Figure 4: Mean monthly variations of U/Ca (red) and $\delta^{13}\text{C}$ (blue) in stalagmite YOK-G (means over 1669-1983). Mean monthly rainfall at the Punta Gorda meteorological station from 1966-1985 (grey bars).

Figure 5: Influence of rainfall on $\delta^{13}\text{C}$ and factors influencing U/Ca ratios in speleothems.

Figure 6: Comparison of mean monthly fluctuations in U/Ca and $\delta^{13}\text{C}$ in years with varying levels of correlation between the two variables. The dataset is divided into six separate groups based on the correlation between U/Ca and $\delta^{13}\text{C}$, then the mean values for each calendar month plotted above. January and December months are labelled, with months joined sequentially.

Figure 7: Comparison of selected decades where $\delta^{13}\text{C}$ and U/Ca are A) seasonally anti-correlated (1790-1800) and B) seasonally correlated (1950-1960). Dashed lines show decadal mean values, with range bars representing \pm one standard deviation. Decadal means suggest that, based on both proxies, the seasonally correlated decades are drier overall, with smaller amplitude seasonal variations.

Figure 8: A) Mean annual $\delta^{13}\text{C}$ vs. seasonal correlation between U/Ca and $\delta^{13}\text{C}$ and B) U/Ca vs. seasonal correlation between U/Ca and $\delta^{13}\text{C}$. C) U/Ca vs. $\delta^{13}\text{C}$ seasonal correlations as an annual time series with 15-year running average. Correlation values shift from negatively correlated towards more positively correlated in recent years.

Figure 9: Competing controls on U/Ca during wet and dry years. During wet years (A, B) PAP is highly variable seasonally (A), dominating the U/Ca intra-annual variability and anti-correlating with $\delta^{13}\text{C}$ (B). During dry years (C, D) PAP is less variable seasonally and the signal is subsumed by bedrock interaction (C), resulting in a seasonal correlation with $\delta^{13}\text{C}$ (D).

Figure 10: Mean monthly variations of Mg/Ca (green) and $\delta^{13}\text{C}$ (blue) in stalagmite YOK-G (means over 1669-1983). Mean monthly rainfall at the Punta Gorda meteorological station from 1966-1985 (grey bars).

Source	Type	n	D_{U}^{a} Min	D_{U}^{a} Max	D_{U}^{a} Mean
Sackett and Potratz (1963)	Aragonitic Corals in Seawater	2	0.62	0.81	0.72
Veeh and Turekian (1968)	Aragonitic Corals in Seawater	8	0.51	0.95	0.72
Friedman (1968)	Aragonitic Corals in Seawater	2	0.76	0.83	0.80
Schroeder et al. (1970)	Aragonitic Corals in Seawater	6	0.64	1.42	1.02
Thompson and Livingston (1970)	Aragonitic Corals in Seawater	4	0.97	1.46	1.30
Gvirtsman et al. (1973)	Aragonitic Corals in Seawater	3	0.61	0.67	0.64
Amiel et al. (1973)	Aragonitic Corals in Seawater	3	1.01	1.01	1.01
Flor and Moore (1977)	Aragonitic Corals in Seawater	4	0.91	1.3	1.05
Swart and Hubbard (1982)	Aragonitic Corals in Seawater	9	0.53	0.87	0.65
DeCarlo et al. (2015)	Abiogenic Seawater Lab Experiment	27 4	0.15	0.38	0.31
Gabitov et al. (2008)	U^{6+} laboratory experiment, inorganic precipitation with ammonium	8 8	0.04	0.15 0	0.12

	carbonate				
Meece and Benninger (1993)	Seawater, high pCO ₂ to saturate with CaCO ₃	11	1.77	9.85	4.11
McDermott et al. (1999)	Vertical Transition				3.52
Railsback et al. (2011)	Vertical Transition				1.95
Wassenburg et al. (2012)	Vertical Transition				1.85
Wassenburg et al. (2012)	Vertical Transition				2.62
Wassenburg et al. (2012)	Vertical Transition				3.09
Mean Value (Vertical Transition)					2.60 ± 0.72
Wassenburg (2013)	Lateral Change				4.55
Wassenburg (2013)	Lateral Change				2.94
Mean Value (Lateral Transition)					3.74 ± 1.13

Table 1: Values of D_V^a used in Figure 1.

	r value	p value
Peak Wet $\delta^{13}\text{C}$	0.42	4.3×10^{-7}
Peak Dry $\delta^{13}\text{C}$	0.40	1.4×10^{-6}
Mean Annual $\delta^{13}\text{C}$	0.46	1.8×10^{-8}
Seasonal Difference in $\delta^{13}\text{C}$	-0.15	0.08
Peak Wet U/Ca	-0.59	2.5×10^{-14}
Peak Dry U/Ca	-0.65	1.3×10^{-17}
Mean Annual U/Ca	-0.68	8.1×10^{-20}
Seasonal Difference in U/Ca	-0.19	0.030
$\delta^{13}\text{C}$ vs U/Ca Correlation	0.34	4.52×10^{-5}

Table 2: Industrial period (1850-1983) correlations and significance of hydrological proxies with the Northern Hemisphere Temperature reconstruction of Esper et al. (2002).